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Number of ways
this can occur $= t_i = \frac{g_i!}{n_i! (g_i - n_i)!}$

Combining all i levels

$$t\{n_i\} = \frac{g_1!}{n_1! (g_1 - n_1)!} \times \frac{g_2!}{n_2! (g_2 - n_2)!} \dots \times \frac{g_i!}{n_i! (g_i - n_i)!}$$
$$= \prod_i \frac{g_i!}{n_i! (g_i - n_i)!}$$

Need maximum of $t\{n_i\}$ - call t

Work with $\ln t$

$$\ln t = \sum_i \ln g_i! - \ln n_i! - \ln (g_i - n_i)!$$

Use Stirling's theorem

$$\ln t = \sum_i g_i \ln g_i - \cancel{g_i} - n_i \ln n_i + \cancel{n_i} - (g_i - n_i) \ln (g_i - n_i) + \cancel{g_i} - \cancel{n_i}$$

Maximize w.r.t n_i

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$$d(\ln t) = \sum_i \left(-\ln n_i - \frac{n_i}{n_i} + \ln(g_i - n_i) + \frac{(g_i - n_i)}{(g_i - n_i)} \right) dn_i$$
$$= \sum_i \ln \left(\frac{g_i - n_i}{n_i} \right) dn_i = 0$$

Conditions.

- (i) Constant particle number N $\sum_i \alpha dn_i = 0$
- (ii) Constant energy U $\sum_i \beta \epsilon_i dn_i = 0$

Incorporate conditions

$$0 = \sum_i \left(\ln \left(\frac{g_i - n_i}{n_i} \right) + \alpha + \beta \epsilon_i \right) dn_i$$

For independent dn_i - solⁿ requires

$$\ln \left(\frac{g_i - n_i}{n_i} \right) + \alpha + \beta \epsilon_i = 0 \quad (\text{all } i)$$

$$\ln \left(\frac{g_i - n_i}{n_i} \right) = -\alpha - \beta \epsilon_i$$

$$n_i = \frac{g_i}{\exp(-\alpha - \beta \epsilon_i) + 1}$$

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Usually written as

$$\text{Prob occupation } f(\epsilon_i) = \frac{n_i}{g_i} = \frac{1}{\exp(-\alpha - \beta \epsilon_i) + 1}$$

With $B = \exp(-\alpha)$ - normalises to particle number

$$\text{and } \beta = -1/kT$$

get

$$f(\epsilon) = \frac{1}{B \exp(\epsilon/kT) + 1}$$

Fermi - Dirac distribution.

Bose Einstein gas } see sheets for
Boltzmann gas } distributions

Bose Einstein Gas.

Distribution.

Again n_i particles in level energy ϵ_i , degeneracy g_i but for bosons multiple occupation of states allowed.

Want number of ways n_i particles can be distributed in g_i states.

Make line of n_i particles.

x x x x x x x x x x x x x x x

Insert bars to break up particles into groups in diff states

x x x | x | | x | x x | | | x | x x x | x | x | | x x | |

particles
per
state

3 1 0 1 2 0 0 1 3 1 1 0 2 0

For g_i states — need $(g_i - 1)$ bars

Different microstates achieved by permuting places of $(n_i + g_i - 1)$ x and bars

Number of microstates for level i $t_i = \frac{(g_i + n_i - 1)!}{(g_i - 1)! n_i!}$

g_i and n_i large numbers — can drop -1.

$$t_i = \frac{(g_i + n_i)!}{g_i! n_i!}$$

Combining all levels.

$$t\{n_i\} = \prod_i \frac{(g_i + n_i)!}{g_i! n_i!}$$

Maximize $t\{n_i\}$

Deal with $\ln t$

$$\ln t = \sum_i \ln(g_i + n_i)! - \ln g_i! - \ln n_i!$$

Use Stirling's approximation

$$\ln t = \sum_i (g_i + n_i) \ln(g_i + n_i) - (g_i + n_i) - g_i \ln g_i + g_i - n_i \ln n_i + n_i$$

Maximize $\ln t$ wrt n_i values.

$$\begin{aligned} d(\ln t) = 0 &= \sum_i \left[\ln(g_i + n_i) + \left(\frac{g_i + n_i}{g_i + n_i} \right) - \ln n_i - \frac{n_i}{n_i} \right] dn_i \\ &= \sum_i \ln \left(\frac{g_i + n_i}{n_i} \right) dn_i \end{aligned}$$

Add constraints on number and energy

$$0 = \sum_i \left(\ln \left(\frac{g_i + n_i}{n_i} \right) + \alpha + \beta \epsilon_i \right) dn_i$$

For independent dvi require

$$\ln \left(\frac{g_i + n_i}{n_i} \right) + \alpha + \beta \epsilon_i = 0$$

$$\ln \left(\frac{g_i + n_i}{n_i} \right) = -\alpha - \beta \epsilon_i$$

$$n_i = \frac{g_i}{\exp(-\alpha - \beta \epsilon_i) - 1}$$

Probability of population

$$f(\epsilon_i) = \frac{n_i}{g_i} = \frac{1}{B \exp(\epsilon_i / kT) - 1}$$

using $B = \exp(-\alpha)$

$$\beta = -1/kT.$$

Bose - Einstein distribution

$$f(\epsilon) = \frac{1}{[B \exp(\epsilon / kT) - 1]}$$

Boltzmann gas.

An important approximation valid when $f(\epsilon_i) = \frac{n_i}{g_i} \ll 1$.

Then distinction between Fermi Dirac and Bose-Einstein becomes unimportant.

For n_i particles in g_i states of level i

Counting microstates (Fermi-Dirac)

$$t_i = \frac{g_i!}{n_i! (g_i - n_i)!} \approx \frac{g_i (g_i - 1) (g_i - 2) \dots (g_i - n_i + 1)}{1 \times 2 \times 3 \dots n_i}$$

for $g_i \gg n_i$

$$t_i \sim \frac{g_i^{n_i}}{n_i!}$$

$$\text{All levels. } t\{n_i\} = \prod_i \frac{g_i^{n_i}}{n_i!}$$

Maximise $\ln t$

$$\ln t = \sum_i n_i \ln g_i - \ln n_i!$$

Using Stirling's approximation

$$\ln t = \sum_i n_i \ln g_i - n_i \ln n_i + n_i$$

Maximise wrt n_i values

$$d(\ln t) = 0 = \sum_i (\ln g_i - \ln n_i - 1 + 1) dn_i$$

Adding in number and energy constraints

$$0 = \sum_i \left(\ln \left(\frac{g_i}{n_i} \right) + \alpha + \beta \epsilon_i \right) dn_i$$

Independent dn_i requires

$$\ln \left(\frac{g_i}{n_i} \right) + \alpha + \beta \epsilon_i = 0$$

$$\ln \left(\frac{g_i}{n_i} \right) = -\alpha - \beta \epsilon_i$$

$$g_i = n_i \exp(-\alpha - \beta \epsilon_i)$$

$$f(\epsilon_i) = \frac{n_i}{g_i} = \frac{1}{\exp(-\alpha - \beta \epsilon_i)}$$

$$f(\epsilon) = \frac{1}{B \exp(\epsilon/kT)}$$

Boltzmann distribution.

Using $B = \exp(-\alpha)$ and $\beta = -1/kT$.

Consider examples of such systems below.

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Study real gas.

Theory - Maxwell Boltzmann gas.

Where

$$(i) f_i = \frac{n_i}{g_i} = \frac{1}{B \exp(\epsilon_i/kT)} = A \exp(-\epsilon_i/kT)$$

$$(ii) f_i \ll 1.$$

Since - as $\epsilon_i \rightarrow 0$

$$\exp(-\epsilon_i/kT) \rightarrow 1$$

require $A \ll 1$.

Program. - for He gas at NTP

$$p = 1 \text{ atmosphere}$$

$$T = 273 \text{ K}$$

(1) Show M-B theory valid

(2) Get distributions of particle speed
particle velocity components

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(3) Derive thermodynamic quantities U , C_v , S , P as functions of T .

(1) Validity — show $A \ll 1$.

$$n_i = g_i A \exp(-\epsilon_i/kT)$$

$$N = \sum_i n_i = A \sum_i g_i \exp(-\epsilon_i/kT) = AZ$$

where Z = partition function

$$\text{Thus } A = \frac{N}{Z}$$

Calc Z — then A

$$Z = \sum_i g_i \exp(-\epsilon_i/kT)$$

for closely spaced energy levels of gas atoms in macroscopic box

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$$Z = \int_0^{\infty} g(k) dk \exp(-\epsilon/kT)$$

using $\epsilon = \frac{h^2 k^2}{8\pi^2 m}$

$$Z = \int_0^{\infty} \frac{4\pi V}{(2\pi)^3} k^2 dk \cdot \exp\left(-\frac{h^2 k^2}{8\pi^2 m kT}\right)$$

$$b = \frac{h^2}{8\pi^2 m kT}$$

Standard integral - see sheet.

$$Z = V \cdot \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \leftarrow \text{partition function}$$

Value of A .

$$A = \frac{N}{Z} = \frac{N}{V} \left(\frac{h^2}{2\pi m kT} \right)^{3/2}$$

Gas at NTP

$$\frac{N}{V} = \frac{6 \times 10^{23}}{22.4 \times 10^{-3} \times 10^{-6}} = 2.7 \times 10^{25} \text{ m}^{-3}$$

He gas

$$m = 4 \times 1.66 \times 10^{-27} \text{ kg}$$

Maxwell - Boltzmann integrals

$$I_n = \int_0^{\infty} x^n \exp(-bx^2) dx$$

Can be evaluated from relations.

$$I_0 = \frac{1}{2} \left(\frac{\pi}{b} \right)^{1/2}$$

$$I_1 = \frac{1}{2b}$$

$$I_n = \left(\frac{n-1}{2b} \right) I_{n-2}$$

For n even.

$$I'_n = \int_{-\infty}^{+\infty} x^n \exp(-bx^2) dx = 2 I_n$$

For n odd

$$I'_n = \int_{-\infty}^{+\infty} x^n \exp(-bx^2) dx = 0$$

$$(66) \quad A = 2.7 \times 10^{25} \left[\frac{(6.63 \times 10^{-34})^2}{2\pi \times 4 \times 1.66 \times 10^{-27} \times 1.38 \times 10^{-23} \times 273} \right]^{3/2}$$

$$A = 4 \times 10^{-6}$$

Thus $A \ll 1$

M-B theory valid.

For He gas at 5 K - just above

Condensation point $A = 0.09$ - here

MB fair - not good approx.

67 Distributions.

Number of particles = no of states \times prob of occupation

$$n_i = g_i \times f_i$$

No particles with

Speed $v \rightarrow v+dv$

$$n(v) dv = g(v) dv \cdot A \exp\left(-\frac{mv^2}{2kT}\right)$$

$$\text{using } \epsilon = \frac{1}{2}mv^2$$

Evaluate $g(v) dv$

$$\text{M-B theory } g(k) dk = \frac{V}{(2\pi)^3} \cdot 4\pi k^2 dk$$

$$\text{Using } mv = \frac{hk}{2\pi}$$

$$k^2 = \left(\frac{2\pi mv}{h}\right)^2$$

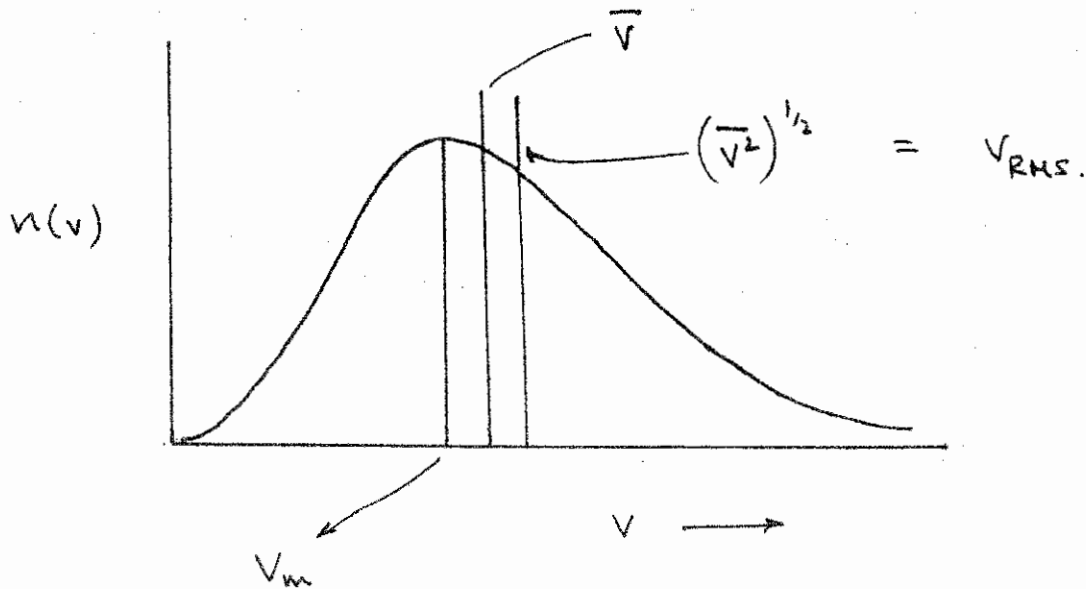
$$dk = \left(\frac{2\pi m}{h}\right) dv$$

get

$$g(v) dv = \frac{V}{(2\pi)^3} \cdot 4\pi \left(\frac{2\pi mv}{h}\right)^2 \left(\frac{2\pi m}{h}\right) dv$$

Maxwell distribution of particle speeds.

$$n(v) dv = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv$$



Particular velocities.

Most probable velocity $v_m = \left(\frac{2kT}{m} \right)^{1/2}$

Mean velocity $\bar{v} = \left(\frac{8kT}{\pi m} \right)^{1/2}$

Root mean square velocity $(\bar{v}^2)^{1/2} = \left(\frac{3kT}{m} \right)^{1/2}$

Such mean energy $\frac{1}{2} m \bar{v}^2 = \frac{3kT}{2}$

Distribution of velocity components.

Number of particles with velocity components in ranges

$v_x \rightarrow v_x + dv_x$, $v_y \rightarrow v_y + dv_y$, $v_z \rightarrow v_z + dv_z$ is

$$n(v_x, v_y, v_z) dv_x dv_y dv_z = g(v_x, v_y, v_z) dv_x dv_y dv_z \cdot A \exp\left(-\frac{mv^2}{2kT}\right)$$

$$\text{where } v^2 = v_x^2 + v_y^2 + v_z^2$$

From above

$$g(k_x, k_y, k_z) dk_x dk_y dk_z = \frac{dk_x dk_y dk_z}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{(2\pi)^3} dk_x dk_y dk_z$$

$$\text{Using } dk_x = \frac{2\pi m}{h} dv_x \text{ etc.}$$

$$g(v_x, v_y, v_z) dv_x dv_y dv_z = \left(\frac{2\pi m}{h}\right)^3 \cdot \frac{V}{(2\pi)^3} dv_x dv_y dv_z$$

Then

$$n(v_x, v_y, v_z) dv_x dv_y dv_z = N \cdot \left(\frac{m}{h}\right)^3 \left(\frac{N}{V}\right) \left(\frac{h^2}{2\pi m kT}\right)^{3/2} \exp\left(-\frac{mv_x^2}{2kT}\right) \exp\left(-\frac{mv_y^2}{2kT}\right) \exp\left(-\frac{mv_z^2}{2kT}\right) \cdot dv_x dv_y dv_z$$

Thus distribⁿ fn is

$$n(v_x, v_y, v_z) dv_x dv_y dv_z = N \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv_x^2}{2kT}\right) \exp\left(-\frac{mv_y^2}{2kT}\right) \exp\left(-\frac{mv_z^2}{2kT}\right) dv_x dv_y dv_z$$

Number particles with x velocity in range $v_x \rightarrow v_x + dv_x$ and any velocity in other directions is

$$n(v_x) dv_x = N \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv_x^2}{2kT}\right) dv_x \int_{-\infty}^{\infty} \exp\left(-\frac{mv_y^2}{2kT}\right) dv_y \int_{-\infty}^{\infty} \exp\left(-\frac{mv_z^2}{2kT}\right) dv_z$$

gives

$$n(v_x) dv_x = N \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{mv_x^2}{2kT}\right) dv_x.$$

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Thermodynamic functions and their variation with temperature T .

(1) Energy U

Use bridge equation

$$U = N \frac{\partial}{\partial \beta} (\ln Z)$$

$$\text{where } \beta = -\frac{1}{kT}$$

$$\text{so } \frac{\partial}{\partial \beta} = kT^2 \frac{\partial}{\partial T}$$

$$U = NkT^2 \frac{\partial}{\partial T} \left(\ln \left[V \cdot \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right] \right)$$

gives

$$U = \frac{3}{2} NkT$$

Energy content $\propto T$.

Derive expression for entropy S

Use bridge equation

$$S = k \ln \Omega \quad \Omega = \text{total no microstates}$$

$$S = k \ln t^* \quad \leftarrow \text{Prob sheet 1.}$$

$$S = k \ln \left\{ \prod_i \frac{(g_i)^{n_i}}{n_i!} \right\} \quad \text{for M-B gas.}$$

$$S = k \left\{ \sum_i n_i \ln g_i - \ln n_i! \right\}$$

$$= k \left\{ \sum_i n_i \ln g_i - n_i \ln n_i + n_i \right\} \quad \text{Stirling's approx}$$

$$= k \sum_i n_i \left(\ln \left(\frac{g_i}{n_i} \right) + 1 \right)$$

Using $f_i = \frac{n_i}{g_i} = \frac{N}{Z} \exp(-\epsilon_i/kT)$ get $\frac{1}{f_i} = \frac{g_i}{n_i} = \frac{Z}{N} \exp(+\epsilon_i/kT)$

$$S = k \sum_i n_i \left(\ln Z - \ln N + \frac{\epsilon_i}{kT} + 1 \right)$$

$$S = k \left(N \ln Z - N \ln N + \frac{U}{kT} + N \right)$$

$$S = Nk \left(\ln Z - \ln N + 1 \right) + \frac{U}{T}$$

This for general gas

For monatomic gas $Z = V \left(\frac{2\pi m k T}{h^2} \right)^{3/2} ; \quad \frac{U}{T} = \frac{3}{2} Nk$

$$S = Nk \left\{ \ln V + \frac{3}{2} \ln T - \ln N \right\} + Nk \left[\frac{3}{2} \ln \left(\frac{2\pi m k}{h^2} \right) + \frac{5}{2} \right]$$

Called Sackur-Tetrode equation. — ok for classical case ^{So}

Can be checked by exp

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(2) Heat Capacity C_v

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = \frac{3}{2} Nk.$$

Predicts C_v constant w.r.t. T

- true at NTP where

$kT \gg \epsilon$ (classical limit).

(3) Entropy S - see sheet.

(4) Pressure P

Use Helmholtz Free Energy F

$$F = U - TS$$

$$= \cancel{U} - NkT(\ln Z - \ln N + 1) - \cancel{U}$$

$$F = -NkT(\ln Z - \ln N + 1)$$

$$F = -NkT \ln Z + kT \ln N!$$

Stirling
reversed.